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Challenges in Nano-Structured Fluid Flows for Assembly into Hierarchical Biomaterials

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Abstract. Hierarchical biomaterials have their place in the context of developing novel material systems particularly in the framework of sustainability. The key to their development is in controlling their assembly into hierarchical orders at various lengthscales. Thus, flow can be an asset in e.g. controlling orientation, however, resolving the hierarchical orientation dynamics of such systems remains a challenge. We focus here mainly on cellulose nanocrystals water-based suspensions, however, the outline is representative of numerous nanostructured fluids.

INTRODUCTION

Hierarchical materials, made up of building blocks covering a range of lengthscales, are ubiquitous in nature [1,2]. In addition to their remarkable properties, hierarchical materials exhibit complex characteristics such as heterogeneity, multifunctionality, environment responsiveness, and self-organization [3]. From biomimetic to bioinspired, such systems have driven an unprecedented level of innovation in materials science [4]. In the context of overarching societal efforts towards increasing the use of renewable resources, abundant polysaccharides such as cellulose and chitin have drawn significant research focus [5]. A common strategy for utilizing such source materials is to break their components down to their smallest constituents and attempt to re-assemble them into new tailored hierarchical materials. Such examples are nanocellulose systems, such as nanofibrils and nanocrystals. In this context, field-nanofiller interactions could hold the key towards the re-assembly of such natural nanofillers into hierarchically structured materials with enhanced properties [6]. In particular, flow-field induced structuring is an extremely advantageous approach because it could unleash a huge potential for efficient mass production in continuous systems [6,7]. Simply solving the issue of dispersion and orientation in the flow direction in nanostructured fluids can result

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in new material functionalities of high performance [8]. However, e.g. for hierarchical nanostructured fluids, their characterization and multiscale control remains a challenge. Of course, resolving hierarchical structures in flow is nothing new. Technically, any nanostructured fluid, be it a suspension or a composite melt, will have a level of hierarchy due to filler agglomeration, i.e. pristine nanoparticles co-exist with agglomerates thereof, which can be further expanded from hierarchical point of view [9]. An interesting complication is if there is a degree of order in mesoscale aggregates, e.g. self-assembly occurs, that is essential for the targeted material properties. This is the case in certain conditions for cellulose and chitin nanocrystals (CNC and ChNC, respectively) as examples of biomaterials [7,11], but also in e.g. graphene oxide suspensions [10], among others. In the sections below several multiscale opportunities and challenges in simple shear flows area outlined. Most of the examples given are based on cellulose nanocrystals and are meant to exemplify some of the challenges associated to controlling their hierarchical structure even in simple shear flows.

FROM SIMPLE TO NOT SO SIMPLE FLOWS

Typically, nanostructured fluid systems lacking any long-range order are referred to as isotropic. Hierarchy in isotropic self-assembling nanostructured fluids stems from the spontaneous formation of mesostructures above a critical concentration when certain nanoparticle interaction conditions are met. Examples of such mesostructures are nematic and chiral nematic local orders are e.g. formed when CNC and ChNC are dispersed in water [7,11]. Thus, at this stage the microstructure comprises unattached pristine particles coexisting with self-assembled domains, i.e. they form a biphasic system. Further increasing nanoparticle concentration will lead to a depletion of the isotropic phase which leads to the formation of a so-called liquid crystalline phase [7]. A fascinating consequence of self-assembly in suspensions lies in their photonic properties, readily observable under polarized light [12]. Figure 1(a) presents such an example using a transmission mode rheo-PLI (rheology combined with polarized light imaging) custom parallel-plate setup visualized at flow-scale [13-16].

Here we wish however to highlight a few challenges in resolving their flow behavior. Firstly, when examining the steady shear viscosity functions of e.g. CNC suspensions, Fig. 1(a), determining at what shear rate are the constituents of such nanostructured fluids oriented in the flow direction is not a trivial matter. In addition, while avoiding elaborated details, we quickly note that in Fig. 1(a) all the viscosity curves were performed on the same CNC grade and that the main difference between them lies in seemingly small details regarding in their preparation procedure (Prep1-4). Further details are beyond the topic of this outline, we briefly note that none of the four preparation protocols used probe sonication. While orientation dynamics have been proposed for a long time for the two viscosity functions that show a three-region behavior [17], recent detailed investigations have yet to fully elucidate their orientation behavior [18].

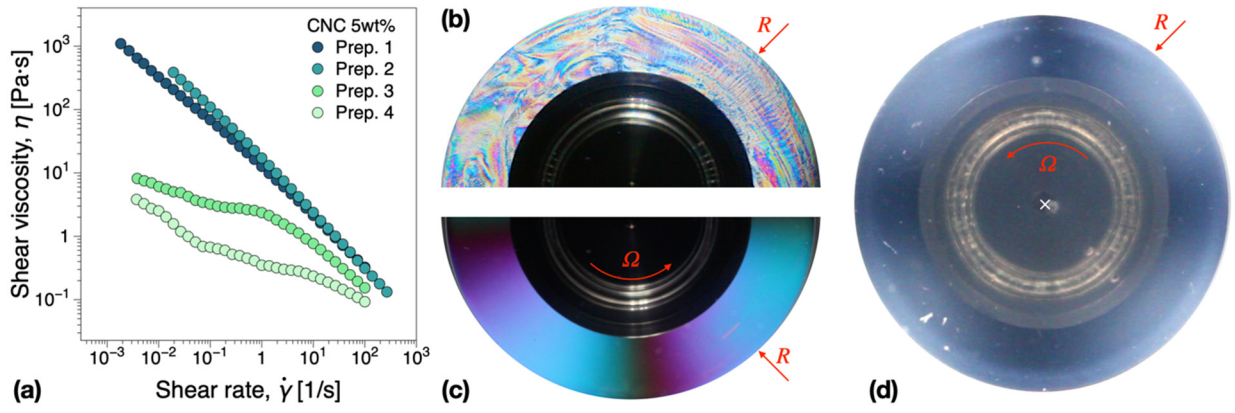

FIGURE 1. (a) Typical shear viscosity functions for biphasic 5 wt% CNC water suspensions. The differences recorded are mainly due to varying sample preparation procedures. (b) PLI optical visualization showing a biphasic 5 wt% CNC suspension between two parallel-plates in the absence of shear flow (visualization from below). (c) Example of the formation of the so-called 'Maltese-cross' pattern, using a similar CNC suspension and measurement setup as in (a), at a shear rate of $\dot{\gamma} = 100\ s^{-1}$. (d) 'Maltese-cross' pattern observed in an aqueous CNF suspension.

However, simultaneous PLI visualizations at flow scale can reveal the co-called 'Maltese-cross' pattern signaling that the main constituents of the suspension generally are oriented in the shear flow direction [19], compare Fig. 1(b) with Fig. 1(c). Maltese-cross patterns can also be used to resolve the orientation at the macroscale of other systems even if they lack self-assembly properties, such as cellulose nanofibrils (CNF) suspensions, see Fig. 1(d). We note that since CNFs lack self-assembly in chiral nematic / nematic domains, the Maltese-cross pattern shows the absence of colors. However, it is important to note that while the orientation at flow scale can be thus determined, this does not resolve the orientation dynamics at all hierarchical levels. It has been shown that during creep measurements, rheo-PLI visualizations at flow scale remained unchanged during the test while rheological data showed evidence of re-structuring [16]. This can be used to emphasize that while rheology captures all the lengthscales of the hierarchy simultaneously, PLI color distortions were related to the larger mesoscale domains. Naturally, probing the smaller lengthscales of the hierarchy requires complementary tests. This can be resolved by performing a rheology combined with e.g. small-angle X-ray scattering experiment, rheo-SAXS, see an example of resulting data in Fig. 2. By comparing the scattering intensity from azimuthal integration as function of the azimuthal angle between a radial, Fig. 2(a)-(c), and a tangential incident beam configuration, Fig. 2(d)-(f), we can assess the orientation state at ~10 nm lengthscales. In the radial configuration (R), incident X-rays are directed through the axis of the concentric cylinder measuring geometry, meaning they are perpendicular to the local velocity and vorticity directions (1-3 plane). Conversely, in the tangential test (T), incident X-rays directed at the middle of the measuring gap, are perpendicular to the local velocity gradient and vorticity directions (2-3 plane), for more details see [7]. Thus, we can see clear orientation peaks in the radial configuration that show a horizontally oriented nanostructure, Fig. 2(a),(c). The peaks are shifted by 90° and are considerably reduced (due to the curvature of the flow the data captures more than orientations in the incident beam direction), Fig. 2(d),(f) thus confirming a unidirectional orientation in the flow direction at the investigated lengthscales. This however does not say necessarily when or how mesoscale domains are structured by flow. The natural extension is therefore to complement macroscopic experiments such as rheo-PLI with nanoscale investigations [18]. Very often such micro-meso-macro correlations can lead to very intriguing results [20]. However, there are also challenges associated to such correlations.

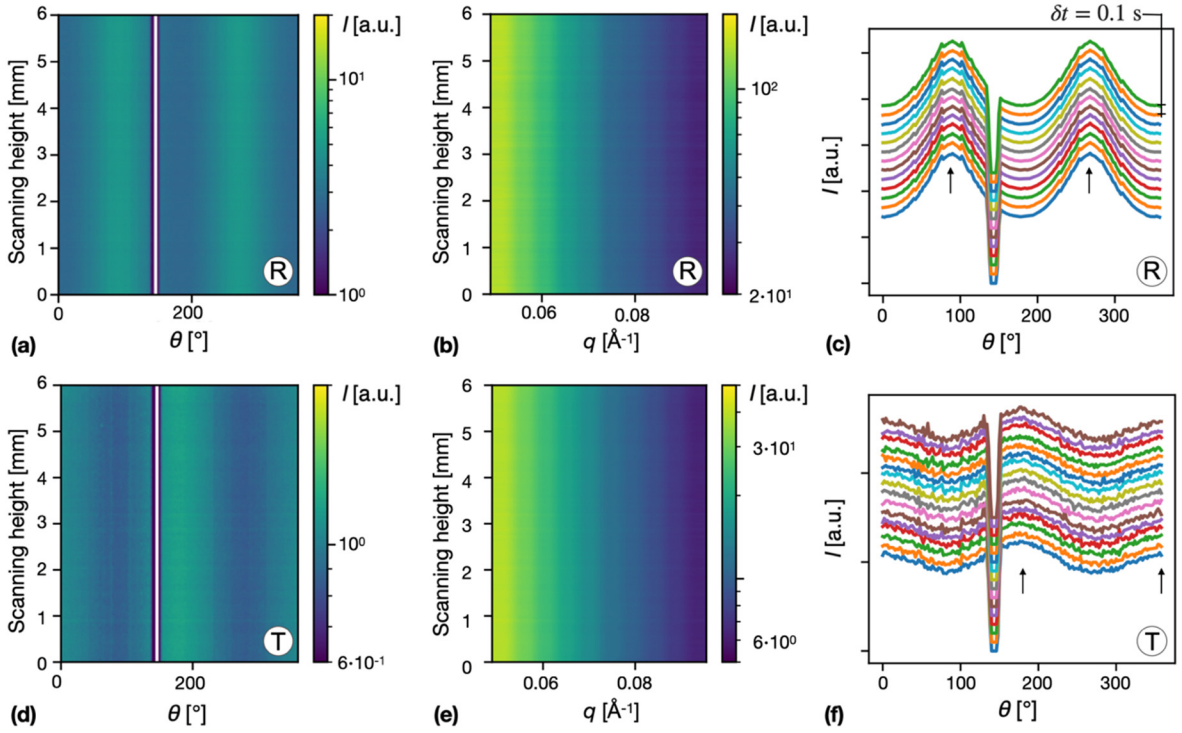

FIGURE 2. (a)-(c) Radial incident beam (R); (d)-(f) Tangential incident beam (T). (a),(d) Scattering intensity colormap plots as function of the scanning height (time averaged 0.5 mm steps). (b),(e) Scattering intensity colormap plots as function of scanning height and azimuthal angle. (e),(f) Scattering intensity vs. azimuthal angle from azimuthal integration with $q \in [5.4,9.5] \cdot 10^{-2}$ Å^{-1} from rheo-SAXS experiments in a cup-bob measuring geometry of a 3 wt% CNC suspension: (a) radial incident beam and (b) tangential incident beam. The curves correspond to successive scans (shifted) every 0.1 s.

In addition to the inherent material variability, the possibility of large errors in material preparation could lead to large differences in the behavior of such nanostructured fluids, Fig. 1(b). Other phenomena can also occur at flow-scale that could further complicate resolving the hierarchical dynamics of such systems. Fascinating yet perhaps unexpected, phenomena especially in biphasic self-assembling systems, seem to be prone to elasticity-driven instabilities [15,11,13]. Such an example is presented in Fig. 3(a). The alternating stripes can be assigned to counter-rotating toroidal vortices travelling in the flow direction [21]. We note that the Reynolds numbers associated to the instabilities in this case are in the range of (10^{-5},10^{-6}) while the Péclet numbers are in the range of (10^{4},10^{5}) [15], and that there is no clear evidence of instabilities in their corresponding viscosity curves. Other challenging structures can also be observed at flow scale in certain particle-particle interactions conditions. Tuning filler-filler interaction could hold the key to unlocking the full potential of nanocellulosic systems, including the possibility of creating structures that can be flow-directed to self-assembly. In the example shown in Fig. 3(b), however, while the viscosity function associated to the measurement was pertinent (data not shown), the agglomeration of the CNC particles was such that they formed rolling cylindrical structures with the rotation axis perpendicular to the flow direction.

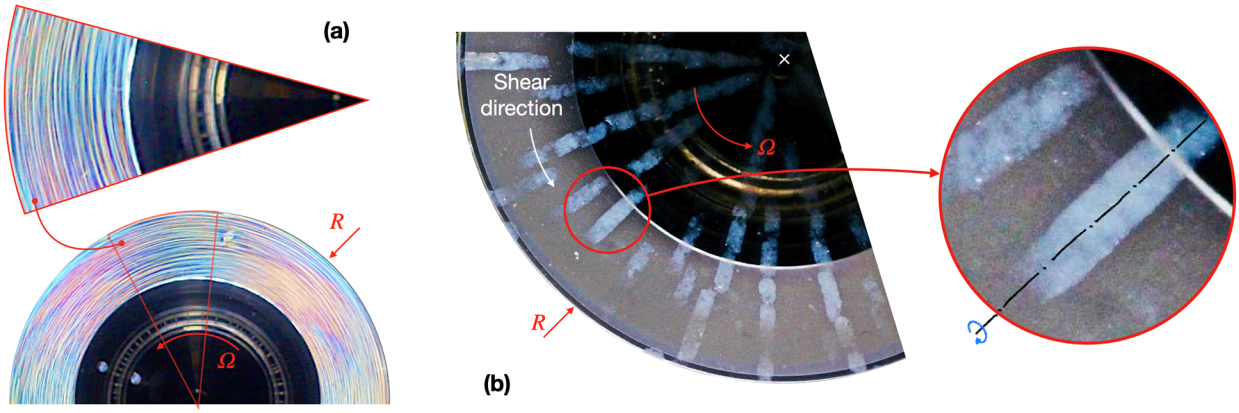

FIGURE 3. (a) Elasticity-driven instabilities in parallel-plate flow of a 5 wt% CNC suspension at a shear rate of ca. $\dot{\gamma} = 0.19\ s^{-1}$. (b) CNC agglomerates flowing as cylindrical agglomerates rolling in the flow direction with the rotation axis perpendicular to the shear direction.

CONCLUSION

While far from exhaustive, several aspects associated to understanding how to structure hierarchical materials through flow have been outlined. Resolving for example orientation dynamics in a hierarchy requires several experiments probing various lengthscales of the hierarchy to avoid erroneous conclusions when probing just the bulk rheological material behavior and / or just one level of the hierarchy. Further challenges that are not outlined here relate to the ability to arrest a flow-induced structure during e.g. drying into coatings and films.

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